

Nuclear Magnetic Resonance Studies of *N*-Vinylcarbazole/Methyl Methacrylate Copolymers

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ABSTRACT: Copolymers of *N*-vinylcarbazole and methyl methacrylate of different compositions were prepared by solution polymerization with azobisisobutyronitrile as an initiator, and their compositions were determined from quantitative $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy. The reactivity ratios for the comonomers were calculated with the Kelen-Tudos and nonlinear error-in-variable methods. The complete spectral assignment of the overlapping ^1H and $^{13}\text{C}\{^1\text{H}\}$

spectra of the copolymers was made with the help of distortionless enhancement by polarization transfer, two-dimensional heteronuclear single-quantum correlation, and total correlation spectroscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3005–3012, 2003

Key words: copolymerization; NMR; microstructure

INTRODUCTION

Poly(*N*-vinylcarbazole) (PVK) has been the subject of intensive investigations because it is one of the most sensitive photoconductive organic polymers.^{1,2} PVK is a stiff, brittle substance with poor mechanical and processing characteristics. Copolymerization with suitable monomers could soften the resulting product, leading to better film properties, and improve its mechanical properties. The copolymerization of *N*-vinylcarbazole with monomers such as alkyl acrylates and alkyl methacrylates has been studied by several investigators.^{3–6}

The determination of the microstructure in copolymers is useful for establishing the structure–property relationship.⁷ It is well known that NMR spectroscopy is probably the most effective method for characterizing the microstructures of polymers.^{8–10} Chiellini et al.⁶ reported the synthesis and optical properties of *N*-vinylcarbazole (V)/methyl methacrylate (M) copolymers, but a literature survey has revealed that the detailed microstructures of these copolymers have not been reported so far.

In earlier publications, we reported the microstructures of *N*-vinylcarbazole/vinyl acetate¹¹ and *N*-vinylcarbazole/methyl acrylate¹² copolymers with one-dimensional (1D) and two-dimensional (2D) NMR spectroscopy. In this article, we report the microstructures

of V/M copolymers with the help of $^{13}\text{C}\{^1\text{H}\}$, distortionless enhancement by polarization transfer (DEPT), 2D heteronuclear single-quantum correlation (HSQC), and total correlation spectroscopy (TOCSY) NMR experiments. The carbonyl, methyl, and methoxy regions of the M unit and the methine region of the V unit in the copolymers are sensitive to triad compositional sequences, and the methylene regions of both the V and M units are sensitive to dyad and tetrad compositional sequences as well as configurational sequences. The reactivity ratios of the comonomers are calculated with the Kelen–Tudos (KT) method¹³ and nonlinear error-in-variable method (EVM).¹⁴

EXPERIMENTAL

V (Aldrich, Milwaukee, WI) was used as supplied, and M (Central Drug House, Pvt., Ltd., New Delhi, India) was distilled under reduced pressure and stored below 5°C. A series of V/M copolymers containing different molar fractions of V (F_V) in the feed were prepared by free-radical solution polymerization with benzene as a solvent and azobisisobutyronitrile as an initiator at 70°C. The specified concentration of the comonomers and benzene were taken in hard glass tubes, and 0.5% azobisisobutyronitrile was added to the reaction mixture. Oxygen was removed by the passage of nitrogen gas, and the tube was sealed and kept in an oil bath maintained at 70°C. The conversion was kept below 10%. The copolymer was precipitated in methanol. The precipitate was dissolved in chloroform, and reprecipitation was occurred again in methanol. The process was repeated five to six times for the removal of unreacted monomer and solvent from the copolymers, and then the copolymers were dried *in vacuo*.

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TABLE I
Copolymer Compositions and Molecular Weight Averages of V/M Copolymers

Sr. No.	f_v	F_v	$M_n \times 10^{-5}$ (g/mole)	$M_w \times 10^{-5}$ (g/mole)	Polydispersity
VM1	0.30	0.16	1.77	3.22	1.81
VM2	0.40	0.24	1.33	3.19	2.40
VM3	0.50	0.27	1.92	3.77	1.96
VM4	0.65	0.38	1.84	3.91	2.13
VM5	0.70	0.47	1.75	3.99	2.28
VM6	0.75	0.53	1.76	4.05	2.30
VM7	0.80	0.62	1.94	3.84	1.98
VM8	0.85	0.68	1.98	3.84	1.94

f_v = the molar fraction of V in the feed; M_n and M_w = number-average and weight-average molecular weights of the copolymers measured by gel permeation chromatography.

All the 1D (^1H , $^{13}\text{C}\{^1\text{H}\}$, and DEPT) and 2D [HSQC and TOCSY (18 ms)] NMR spectra of the copolymers were recorded in CDCl_3 (Merck, KgaA, Darmstadt, Germany) on a Bruker 300-MHz DPX spectrometer at 25°C , at a concentration of 10–15% (w/v), with standard pulse sequences, as reported in our earlier articles.^{15,16} DEPT measurements were carried in CDCl_3 with a standard pulse sequence, with a J modulation time of 3.7 ms ($J_{\text{CH}} = 135$ Hz) and a 2-s delay time. The 2D HSQC was recorded in CDCl_3 with a standard pulse sequence. A total of 32 scans were accumulated,

with a relaxation delay of 2 s for each of the 512 t_1 experiments. The 2D TOCSY experiments were carried out in CDCl_3 with a standard pulse sequence with a mixing time of 18 ms. The copolymer composition was determined experimentally by quantitative $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy with an inverse-gated decoupling pulse program with a relaxation delay of 10 s. The molecular weight averages were determined by gel permeation chromatography in tetrahydrofuran solutions with polystyrenes as narrow standards on a Waters Associated liquid chromatograph (Mil-

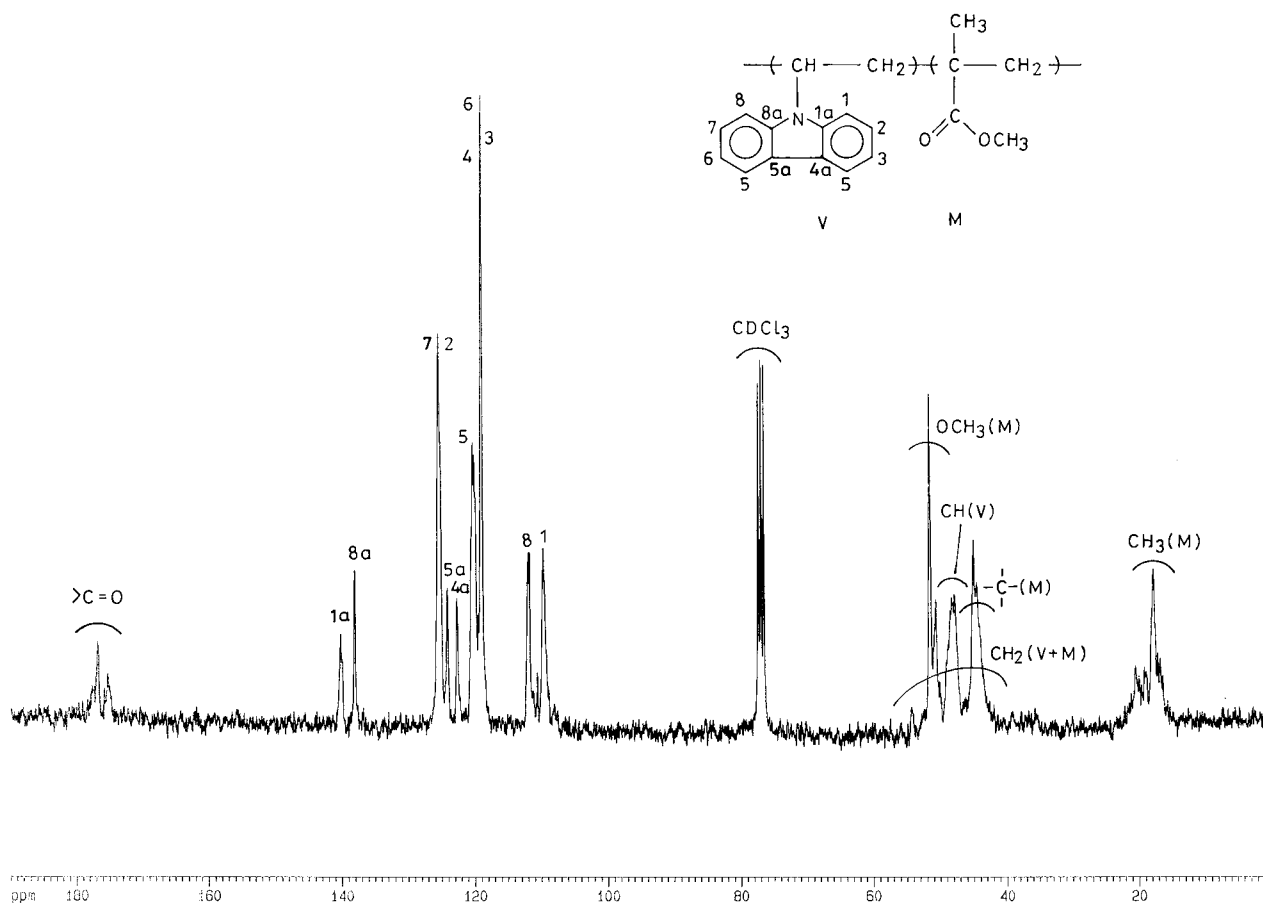


Figure 1 $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of a V/M copolymer ($F_v = 0.38$).

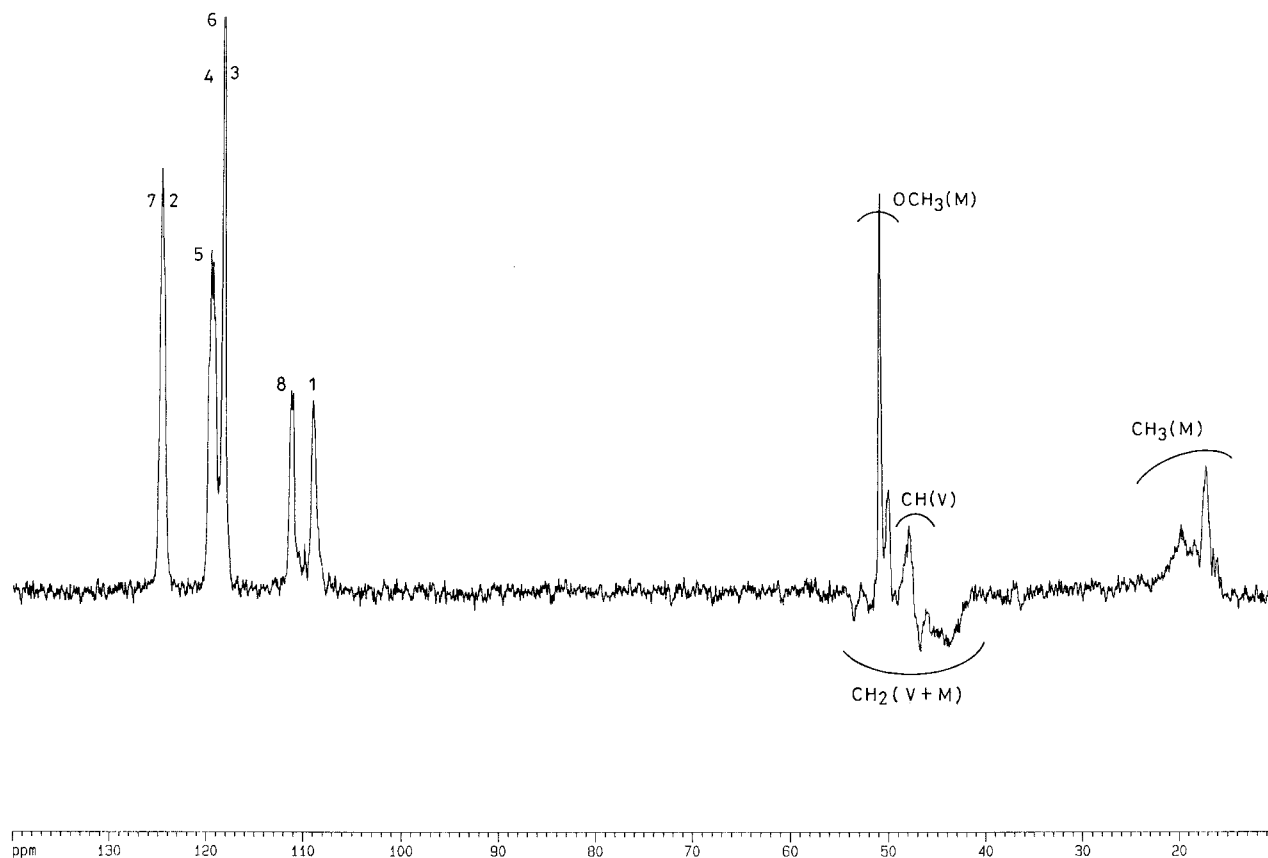


Figure 2 DEPT-135 NMR spectrum of a V/M copolymer ($F_V = 0.38$).

ford, MA) (which consisted of Ultrastyrigel permeation columns, a 501 HPLC solvent delivery system, and an R-400 refractive-index detector).

RESULTS AND DISCUSSION

Reactivity ratio determination

The compositions of the V/M copolymers were determined from quantitative $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra. The comonomer molar fractions in the feed and in the copolymer and the molecular weight averages are shown in Table I. The copolymer composition data were used to calculate the terminal model reactivity ratios with the KT method.¹³ These reactivity ratio values, along with the copolymer composition data, were used to calculate the reactivity ratios from the EVM program.¹⁴ The reactivity ratios obtained from KT and EVM are $r_V = 0.28 \pm 0.09$ and $r_M = 2.11 \pm 0.44$ and $r_V = 0.28$ and $r_M = 2.12$, respectively.

$^{13}\text{C}\{^1\text{H}\}$ -NMR spectral results

The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of the V/M copolymer ($F_V = 0.38$) is shown in Figure 1 along with the complete signal assignments. The carbonyl carbon of the M unit resonates around $\delta = 173.0$ – 178.5 ppm. The aromatic

carbons of the V unit resonate at $\delta = 109.5$ (C-1), 110.5 (C-8), 117.0–119.5 (C-3, 6, 4), 120.3 (C-5), 122.5 (C-4a), 124.0 (C-5a), 124.5–126.0 (C-2, 7), 137.8 (C-8a), and 140.0 ppm (C-1a). These assignments were made with the help of the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of the homopolymers.

The spectral region around $\delta = 14.5$ – 24.0 ppm can be assigned to the methyl carbon resonances of the M unit. The spectral region around $\delta = 42.0$ – 60.0 ppm is quite complex and overlapped and can be assigned to the aliphatic carbons in the main and side chains of the copolymer. To separate the signals in this region, we recorded the DEPT-135 NMR spectrum ($F_V = 0.38$) shown in Figure 2, in which methylene carbon signals appear in the negative phase and methine and methyl carbon signals appear in the positive phase. The methoxy region of the M unit resonates around $\delta = 49.0$ – 52.0 ppm, and the methine region of the V unit in the copolymer resonates around $\delta = 47.5$ – 49.0 ppm. This was also confirmed with the DEPT-90 NMR spectrum. The β -methylene regions of both the M and V units extend from $\delta = 41.0$ to $\delta = 54.5$ ppm.

The carbonyl and methyl carbon resonances of the M unit of the copolymer are sensitive to triad compositional sequences. The expanded spectra of the carbonyl carbon of the M unit in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of V/M copolymers of different feed compositions

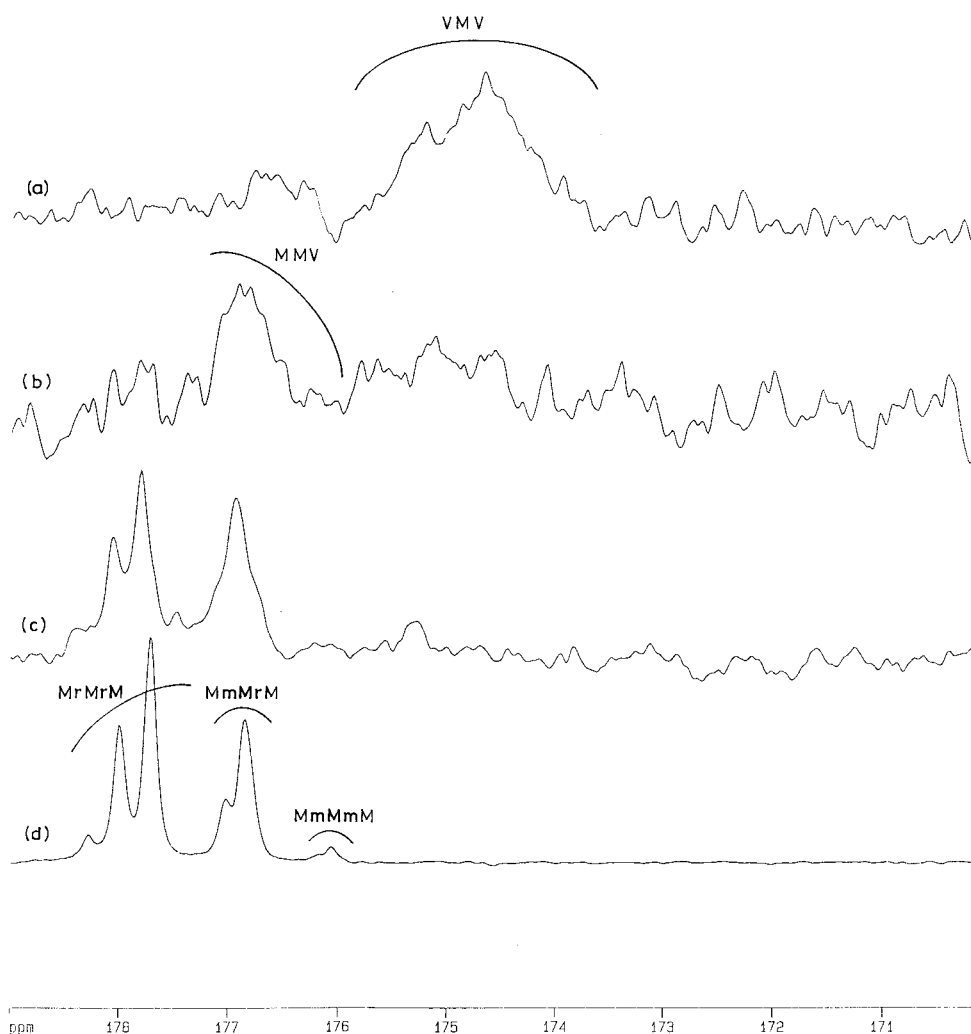


Figure 3 Expanded $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra showing the carbonyl carbon resonance signals of the M unit of V/M copolymers with the following compositions: (a) $F_V = 0.68$, (b) $F_V = 0.38$, (c) $F_V = 0.16$, and (d) poly(methyl methacrylate).

and the corresponding homopolymer are shown in Figure 3(a–d). The signals resonating around $\delta = 175.8$ – 178.5 ppm decrease in intensity with decreases in the M content, the signals resonating around $\delta = 176.0$ – 177.3 ppm first increase and then decrease in intensity with decreases in the M content, and the signals resonating around $\delta = 173.7$ – 176.0 ppm increase in intensity with decreases in the M content. Therefore, on the basis of these changes in the intensities of the signals with changes in the copolymer composition, the three resonating signals around $\delta = 176.5$ – 178.5 , $\delta = 175.3$ – 177.2 , and $\delta = 173.2$ – 175.3 ppm are assigned to the MMM, MMV, and VMV triads, respectively. The spectral regions around $\delta = 177.5$ – 178.5 , $\delta = 176.6$ – 177.3 , and $\delta = 175.8$ – 176.4 ppm are assigned to the configurational sequences MrMrM, MmMrM, and MmMmM, respectively, by comparison with the carbonyl region of the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of poly(methyl methacrylate). Similarly, the expanded methyl carbon region in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of copolymer samples of different feed compositions and poly(methyl methacrylate) are

shown in Figure 4(a–d). The signals resonating around $\delta = 16.0$ – 17.0 , $\delta = 18.4$ – 19.3 , and $\delta = 20.8$ – 21.4 ppm are assigned to MrMrM, MmMrM, and MmMmM configurational sequences, respectively, by comparison with the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra of poly(methyl methacrylate). The signals resonating around $\delta = 16.8$ – 18.4 ppm first show an increase and then decrease in intensity with a decrease in the M content in the copolymers and are, therefore, assigned to MMV triad compositional sequences; the signals resonating around $\delta = 18.3$ – 21.0 ppm show an increase in intensity with a decrease in the M content in the copolymers and are, therefore, assigned to VMV triad compositional sequences. These assignments in the methyl carbon region of the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra are further confirmed by the 2D HSQC spectra.

2D HSQC NMR spectral studies

The expanded HSQC NMR spectra of the methyl region of V/M copolymers are shown in Figure 5(a–c) ($F_V = 0.16, 0.38$, or 0.68), and the data are collected in

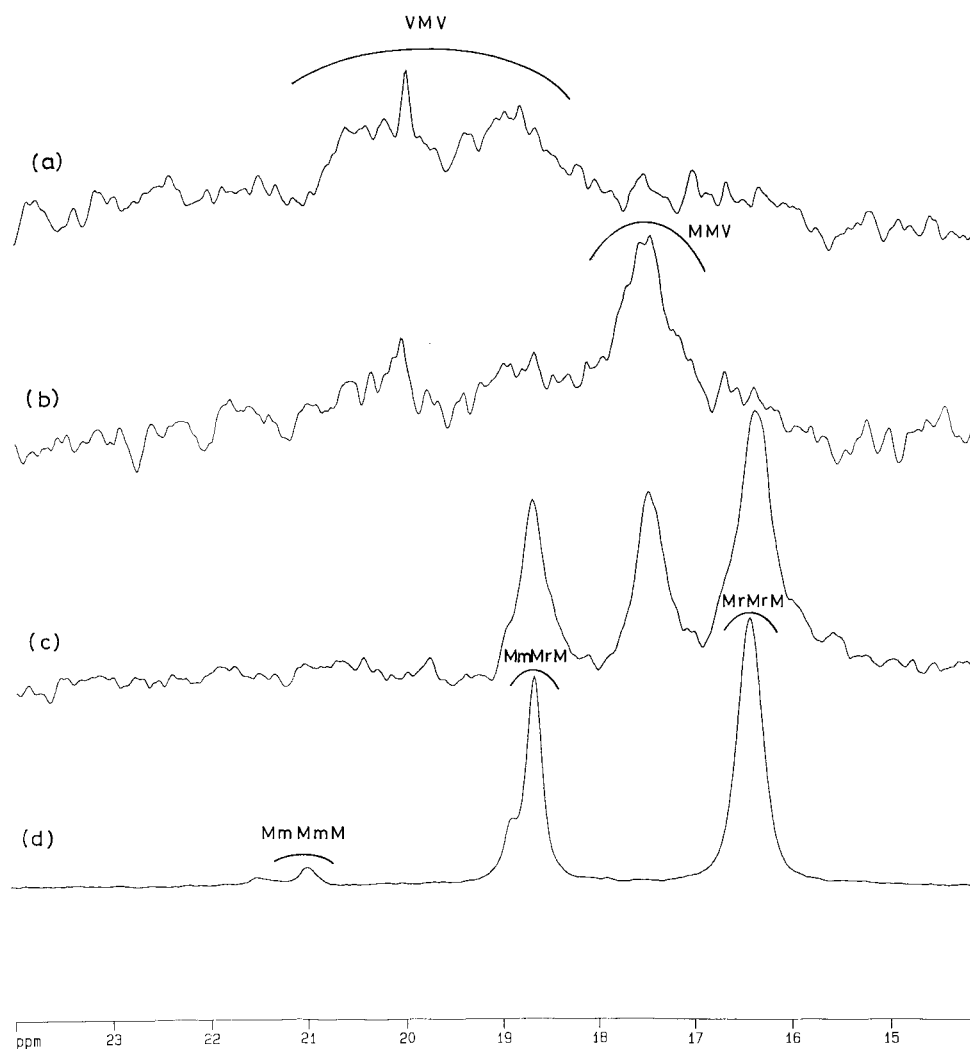


Figure 4 Expanded $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra showing the methyl carbon resonance signals of the M unit of V/M copolymers with the following compositions: (a) $F_V = 0.68$, (b) $F_V = 0.38$, (c) $F_V = 0.16$, and (d) poly(methyl methacrylate).

Table II along with the complete signal assignments. The methyl region shows both compositional and configurational sensitivity. The cross peaks at $\delta = 16.5/0.85$, $\delta = 18.7/1.05$, and $\delta = 21.0/1.20$ ppm are assigned to MrMrM, MrMmM, and MmMmM, respectively, by comparison with the HSQC NMR spectrum of the methyl region of poly(methyl methacrylate). The cross peaks around $\delta = 16.5\text{--}18.5/0.18\text{--}0.55$ ppm and the cross peaks around $\delta = 18.0\text{--}21.5/0.05\text{--}0.40$ ppm are assigned to MMV and VMV compositional sequences on the basis of changes in the intensity with changes in the copolymer composition.

The expanded aliphatic regions of the HSQC spectra showing the methoxy, methine, and β -methylene regions of V/M copolymers are shown in Figure 6(a–c) ($F_V = 0.16$, 0.38, or 0.68). The methine group in the V unit shows compositional sensitivity. The cross peaks around $\delta = 47.5/4.75$, $\delta = 48.0/4.40$, and $\delta = 48.5/3.75$ ppm are assigned to triad compositional sequences MVM, MVV, and VVV, respectively, on the basis of

changes in the intensity with changes in the copolymer composition and the assignments made in the PVK HSQC spectrum. The methoxy region of the M unit shows triad compositional sensitivity along the proton axis. The cross peaks in the region around $\delta = 51.0\text{--}53.0/3.0\text{--}3.7$, $\delta = 49.5\text{--}52.0/2.3\text{--}3.0$, and $\delta = 49.0\text{--}52.0/1.6\text{--}2.3$ ppm are assigned to triad compositional sequences MMM, MMV, and VMV on the basis of changes in the intensity with changes in the copolymer composition and the assignments made in the poly(methyl methacrylate) HSQC spectrum.

The β -methylene group shows both compositional and configurational sensitivity. This region is quite complex and overlapped in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectra but can be resolved with the help of HSQC spectra. The meso configuration of the MM dyad gives two cross peaks due to two methylene protons with different environments, and the racemic configuration gives one cross peak between these two cross peaks. Therefore, the cross peaks centered at $\delta = 54.5/2.00$

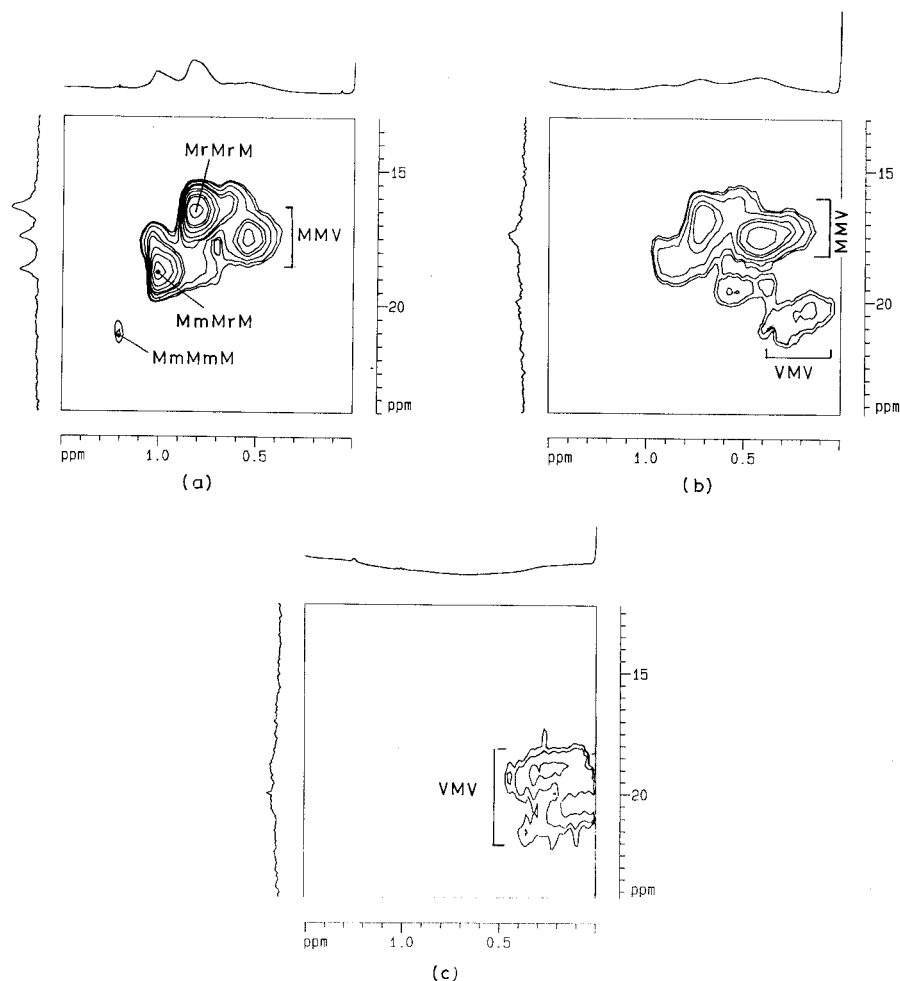


Figure 5 Expanded HSQC spectra showing the methyl region of the M unit of V/M copolymers with the following compositions: (a) $F_V = 0.16$, (b) $F_V = 0.38$, and (c) $F_V = 0.68$.

and $\delta = 54.5/1.75$ ppm are assigned to the MmM dyad, and the cross peak centered at $\delta = 52.5/1.90$ ppm is assigned to the MrM dyad, as shown in Figure 6(a), by comparison with the β -methylene region of the HSQC NMR spectrum of the homopolymer. The MV dyad region is found at $\delta = 40.0\text{--}49.5/1.3\text{--}3.0$ ppm and shows further splitting along both the carbon and proton axes. The splitting along the carbon axis is divided into MV-centered tetrad compositional sequences, whereas along the proton axis, this region shows configurational sensitivity. The region at $\delta = 47.0\text{--}49.0/1.3\text{--}3.0$ ppm is assigned to the MMVM tetrad; along the proton axis, the meso configuration of the MMVM tetrad gives two cross peaks due to two methylene protons with different environments, and the racemic configuration gives one cross peak between these two cross peaks. Therefore, the cross peaks centered at $\delta = 48.5/2.90$ and $\delta = 48.5/1.65$ ppm are assigned to MMmVM, and the cross peak centered at $\delta = 48.5/2.25$ ppm is assigned to MMrVM, as shown in Figure 6(a). The region at $\delta = 42.5\text{--}45.0/1.4\text{--}2.3$ ppm is assigned to the MMVV and VMVM

tetrads, and the region at $\delta = 40.0\text{--}42.5/1.3\text{--}2.2$ ppm is assigned to the VMVV tetrad. There is some splitting along the proton axis in these regions, but it is difficult to accurately assign various configurational sequences. The VV dyad resonates in the region $\delta = 35.5\text{--}39.5/1.6\text{--}2.4$ ppm. These assignments are confirmed by a comparison of HSQC spectra of copolymers of various compositions and those of corresponding homopolymers.

2D TOCSY NMR spectra studies

To understand the connectivity between the different protons and to confirm the various couplings in the polymer chain, we recorded the TOCSY spectra of copolymers of various compositions. The expanded TOCSY spectrum (18 ms), showing the methine and β -methylene regions of the V/M copolymers ($F_V = 0.16$ or 0.68), are shown in Figure 7(a,b), and data are collected in Table III along with the complete signal assignments. The vicinal couplings between the methine protons in V-centered triads with the β -methyl-

TABLE II
Assignments of the Resonance Signals
of the 2D HSQC NMR Spectra

Signal	Peak assignment	Peak positions/ppm
1	(CH ₃) _M	
2	MrMrM	16.5/0.85
3	MmMrM	18.7/1.05
4	MmMmM	21.0/1.20
5	MMV	16.5–18.5/0.18–0.55
6	VMV	18.0–21.5/0.05–0.40
7	(CH) _V	
8	MVM	47.5/4.75
9	VVM	48.0/4.40
10	VVV	48.5/3.75
11	(OCH ₃) _M	
12	MMM	51.0–53.0/3.0–3.7
13	MMV	49.5–52.0/2.3–3.0
14	VMV	49.0–52.0/1.6–2.3
15	(CH ₂) _M	
16	MMmVM(a)	48.5/2.90
17	MMrVM	48.5/2.25
18	MMmVM(b)	48.5/1.65
19	MMVV + VMVM	42.5–45.0/1.4–2.3
20	VMVV	40.0–42.5/1.3–2.2
21	MmM(c)	54.5/2.00
22	MrM	52.5/1.90
23	MmM(d)	54.5/1.75
24	VV	35.5–39.5/1.6–2.4

ene protons in various dyads can clearly be seen in the TOCSY spectra. The methine protons in the MVV triad show coupling with the β -methylene protons of the MV dyad, and this results in the three cross peaks centered at $\delta = 4.55/2.90$ (1), $\delta = 4.55/2.20$ (2), and $\delta = 4.55/1.60$ (3) ppm. These cross peaks do not show any relative changes in intensity with the change in composition and are, therefore, assigned to the coupling of MVV with MmV (a), MrV, and MmV (b) sequences, respectively. Similarly, the cross peaks centered at $\delta = 4.75/1.65$ (4), $\delta = 4.75/2.85$ (5), and $\delta = 4.75/2.25$ (6) ppm are due to the coupling of the methine protons in the MVM triad with the β -methylene protons in the MmV (a), MrV, and MmV (b) sequences, respectively. The cross peak around $\delta = 3.50$ – $3.95/1.80$ – 2.40 (7) ppm is assigned to the coupling of the methine protons in the VVV triad with the β -methylene protons in the VV dyad. The cross peaks centered at $\delta = 2.65$ – $3.00/1.40$ – 1.80 (8) can be assigned to the four-bond coupling between β -methylene protons of the MV dyad and the β -methylene protons of the MM dyad and also to the geminal coupling between the two nonequivalent protons (a

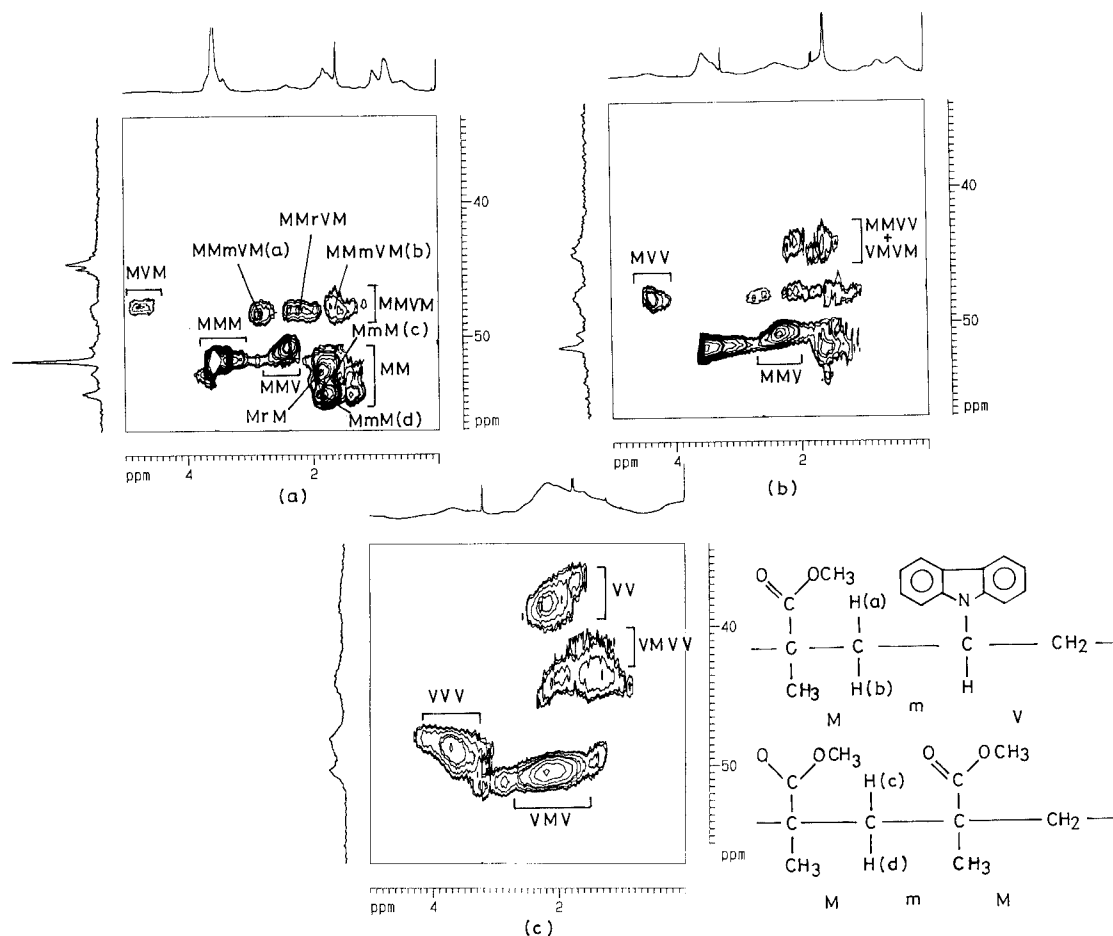


Figure 6 Expanded HSQC spectra showing the methoxy, methine, and β -methylene regions of V/M copolymers with the following compositions: (a) $F_V = 0.16$, (b) $F_V = 0.38$, and (c) $F_V = 0.68$.

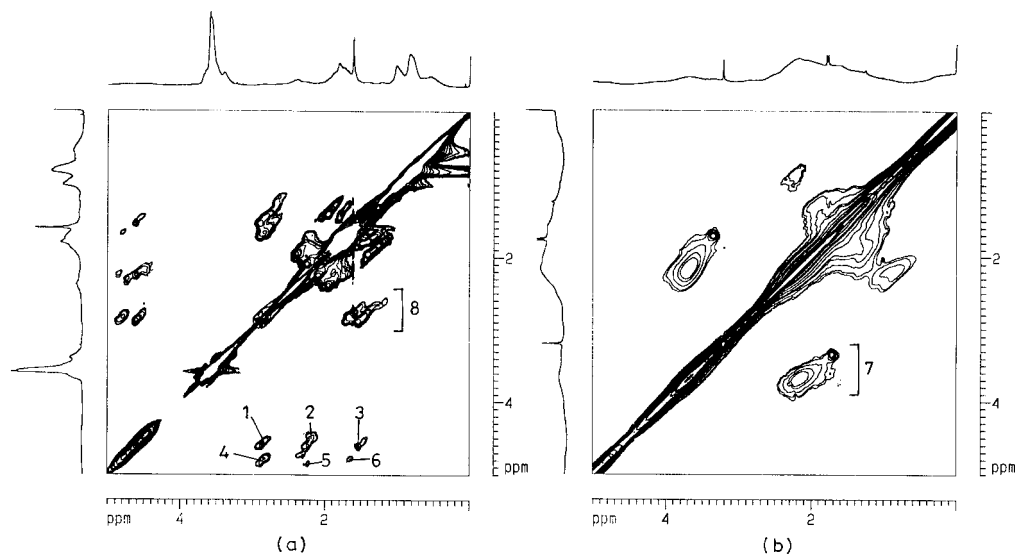


Figure 7 Expanded TOCSY spectra showing the methine and β -methylene regions of V/M copolymers with the following compositions: (a) $F_V = 0.16$ and (b) $F_V = 0.68$.

and b) in the MmV dyad. These assignments are confirmed by a comparison of the TOCSY NMR spectra of copolymers of various compositions and those of the corresponding homopolymers.

CONCLUSIONS

The monomer reactivity ratios of V/M copolymers were found to be $r_V = 0.28 \pm 0.09$ and $r_M = 2.11 \pm 0.44$ from KT and $r_V = 0.28$ and $r_M = 2.12$ from EVM. NMR spectroscopy techniques (DEPT, HSQC, and TOCSY) were used to resolve the overlapping proton and carbon resonance signals of these copolymers completely.

TABLE III
TOCSY ^1H - ^1H Shift Correlation

Peak	Type of proton (ppm)	Coupled to (ppm)
Couplings between		
1	CH in MVV triad (4.55)	β -CH ₂ in MmV(a) dyad (2.90)
2	CH in MVV triad (4.55)	β -CH ₂ in MrV dyad (2.20)
3	CH in MVV triad (4.55)	β -CH ₂ in MmV(b) dyad (1.60)
4	CH in MVM triad (4.75)	β -CH ₂ in MmV(a) dyad (2.85)
5	CH in MVM triad (4.75)	β -CH ₂ in MrV dyad (2.25)
6	CH in MVM triad (4.75)	β -CH ₂ in MmV(b) dyad (1.65)
7	CH in VVV triad (3.50–3.95)	β -CH ₂ in VV dyad (1.80–2.40)
8	β -CH ₂ in MV dyad (2.65–3.00) + geminal coupling between a and b	β -CH ₂ in MM dyad (1.40–1.80)

The carbonyl and methyl resonance signals of the M unit were assigned to triad compositional and configurational sequences. The methoxy carbon resonance signals of the M unit and the methine carbon resonance signals of the V unit were assigned to triad compositional sequences, and the methylene carbon resonances were assigned to dyad and tetrad compositional and configurational sequences.

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